

Problem of formation of an emf in a semiconductor and its transfer to an external circuit

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((Submitted April 4, 1991; accepted for publication May 14, 1991))

A general description is given of a process of formation of an emf in a medium with nonequilibrium carriers. The appearance of anomalous emfs is predicted for several semiconductor structures. Such emfs appear as a result of photogeneration of the majority carriers or, for example, due to homogeneous heating of electrons and holes along the whole circuit. An analysis is made of the problem of determination of an emf inside a multicomponent medium and of recording it in an external circuit.

Many effects associated with the appearance of an electromotive force (emf) are among the topics investigated in semiconductor physics. An emf may appear in a special structure or in a homogeneous sample of finite dimensions.^{1,2} A theoretical description of various emfs is usually based on models postulating some specific mechanisms of the appearance of an electric current and consequently different methods of calculation of the emf are used (see, for example, Refs. 3–5). An increase in the range of the investigated phenomena and the development of new semiconductor structures have made it possible to refine the mechanisms used to account for the observed emfs.^{6,7} However, there is as yet no general description of the process of formation of an emf in a medium containing nonequilibrium carriers. In view of the absence of a general treatment of the problem of how and because of what an emf appears, it is usual to refer to the action of various “external forces of nonelectrical origin,” for example, chemical forces. However, such a statement explains nothing, because it does not show how, in principle, a thermodynamic nonequilibrium gives rise to “external forces” and to an electric current in a closed electrical circuit (if it does at all) and consequently how we can calculate a possible emf in the case of an arbitrary nonequilibrium medium. The conclusion that in a nonequilibrium inhomogeneous circuit the sum of the “contact potentials due to different carriers” may differ from zeros simply clouds the picture, since an electrical potential is the same for all the carriers and the net change of the potential along the complete circuit is always zero, and it is not clear what do the partial contact potentials of different carriers represent and how to calculate them. The examples used to illustrate such conclusions (see Refs. 1–3 and 8) usually deal only with those situations in which the terms introduced can be given a very simple meaning (when the partial contact potentials in some regions can be reduced to differences between chemical potentials).

This means that the problem of formation of an emf must be investigated more thoroughly. This is particularly important in the case of a medium which contains many types of charge carrier particularly when the energy distributions of these carriers are far from equilibrium and the medium is spatially inhomogeneous. Such situations are very typical of semiconductor structures in which electrons and holes are readily excited by external stimuli (for example, they may be heated by an electric field) and the appearance of any unexpected (and, therefore, ignored) emfs in such cases may be of considerable importance. For example, in studies of the transport of hot electrons in microstructures the electric field is usually regarded as given,⁹ whereas in reality we can expect the appearance of emfs that alter the spatial distribution of the field, so that its distribution must be determined in a self-consistent manner allowing also for possible emfs.

The present paper develops a general system of concepts on the process of formation of an emf in arbitrary conducting structures with different nonequilibrium carriers, which would make it possible to calculate correctly emfs of very different origins in a great variety of situations, and to study the problem of how to transfer the resultant emf to an external electrical circuit.

We shall consider a closed circuit formed by a conducting material of unit cross-sectional area. We shall assume that an electric current in this circuit is created by charge carriers of N types and each type of carrier is characterized by its own quasi-Fermi level F_k , temperature T_k , electrical conductivity σ_k , and thermoelectric power α_k ($k = 1, 2, \dots, N$). The partial currents of carriers in such an electrical circuit are described by the expressions 3

$$j_k = -\sigma_k \left(\frac{d}{dx} \tilde{\varphi}_k + \alpha_k \frac{d}{dx} T_k \right), \quad (1)$$

where d/dx is the derivative with respect to the coordinate along the circuit; $\tilde{\varphi}_k = F_k/e_k = \varphi + \mu_k/e_k$ is the electrochemical potential of carriers of the k th type (we shall consider here only the potential electric fields $\mathcal{E} = -\nabla\varphi$); μ_k is the chemical potential of the subsystem of carriers of the k th type. The total current j is the sum of the currents j_k . Under steady-state conditions the total current remains constant along the whole circuit because of the condition

of continuity. Then, the emf in such a close circuit can be described naturally by $E = jR$, where $R = \oint dx/\sigma$ is the total electrical resistance of the circuit and the conductivity is $\sigma = \sum_{k=1}^N \sigma_k$. The relationship $E = jR$ then describes Ohm's law for a closed circuit. If we allow for Eq. (1), we find this relationship leads to the following general expression for the emf:

$$E = - \oint \sum_{k=1}^N \frac{\sigma_k}{\sigma} \left(\frac{d}{dx} \tilde{\varphi}_k + \alpha_k \frac{d}{dx} T_k \right) dx \quad (2)$$

where the integral is taken along the conducting circuit.

Equation (2) represents the most general description¹⁰ of the appearance of an emf in a closed electrical circuit due to the presence of carriers which are not in thermodynamic equilibrium. Obviously, the emf appears when this integral is not a total differential.^{2,11} However, the actual conditions under which this takes place depend on the nature of the conducting circuit and the nature of carrier nonequilibrium.

In the case of a circuit with unipolar conduction ($N = 1$), which is in an inhomogeneous temperature field $T = T(x)$, the relevant conditions are described in detail in Ref. 11. We shall consider other possible situations.

We shall begin with the appearance of an emf in the absence of thermal effects. It follows from Eq. (2) that if $T_k = \text{const}$, then in a medium containing carriers of one kind, we have $E = 0$. This means that, irrespective of whether the circuit with unipolar conduction is homogeneous or inhomogeneous and irrespective of any inhomogeneity of the generation of nonequilibrium carriers (of a given kind), if $T_k = \text{const}$ ($k = 1$), no emf appears in the circuit (see also Refs. 2 and 11). It should be stressed that this conclusion is essentially related to the hypothesis that the symmetric part of the distribution function of carriers is of the Fermi type, so that Eq. (1) applies.

The situation is different in a circuit which contains carriers of several kinds. For example, in the case of a circuit with carriers of two kinds (usually with opposite signs), if $T_k = \text{const}$ ($k = 1, 2$), we have

$$E = \oint \frac{\sigma_1}{\sigma} \frac{d}{dx} (\tilde{\varphi}_2 - \tilde{\varphi}_1) dx = \oint \frac{\sigma_2}{\sigma} \frac{d}{dx} (\tilde{\varphi}_1 - \tilde{\varphi}_2) dx \quad (3)$$

or in the absence of an electrical potential φ , the corresponding expression is

$$E = \oint \frac{\sigma_1}{\sigma} \frac{d}{dx} \left(\frac{\mu_2}{e_2} - \frac{\mu_1}{e_1} \right) dx = \oint \frac{\sigma_2}{\sigma} \frac{d}{dx} \left(\frac{\mu_1}{e_1} - \frac{\mu_2}{e_2} \right) dx \quad (4)$$

In this case (when the temperature of carriers is constant) an emf appears when, firstly, $\psi = (\mu_2/e_2 - \mu_1/e_1) \neq \text{const}$ [for example, in the case of a nondegenerate semiconductor this means that the densities of nonequilibrium carriers δn_1 , and δn_2 are not related by

$$\delta n_2(x) = [C - \delta n_1(x) n_i^2(x)/n_{01}(x)] [n_{01}(x) + \delta n_1(x)], \quad (5)$$

where $n_i(x)$ is the intrinsic equilibrium density, $n_{01}(x)$ is the equilibrium density of carriers of the first kind, and C is an arbitrary constant] and, secondly, $\sigma_1(x)/\sigma_2(x) \neq \text{const}$ (inhomogeneous medium), where σ_1/σ_2 varies along the circuit so that the integrand is no longer a total differential.

It is obvious that these conditions for the appearance of an emf [appropriate nonequilibrium and inhomogeneity of the medium, and the ambipolar conduction ($N = 2$)] represent, in particular, the familiar conditions which are necessary for the generation of a photo-emf in solar cells (see also Ref. 2). When these conditions (or analogous conditions in the case when $N > 2$) are satisfied, we can expect also operation of galvanic ("chemical") sources of the current. If in a circuit with such a source the value of ψ varies from ψ_{\min} to ψ_{\max} and then from ψ_{\max} to ψ_{\min} in sections a and b , respectively, where $\sigma^a = \sigma_1^a$ is the electrical conductivity of electrons and $\sigma^b = \sigma_2^b$ is the electrical conductivity of ions, then the emf will be equal to its maximum possible value $E \approx \psi_{\max} - \psi_{\min}$.

Less obvious, compared with the preceding result, is the conclusion that follows from Eq. (3) that an emf can appear in a unipolar semiconductor containing several types of carriers of the same sign (when $T_k = \text{const}$). Let us consider, for example, a p -type semiconductor with two hole subbands (containing light and heavy holes) where the ratio of the mobilities depends on the coordinate. If in a certain part of this semiconductor we create nonequilibrium holes in one of the subbands, the diffusion of these holes gives rise to a space charge and creates an associated electric field. This field gives rise to an opposite drift current of both light and heavy holes which in the open-circuit case compensates fully the diffusion current. These processes occur on both sides of the region with an excess hole density. If the ratio of the mobilities of the light and heavy holes has different values on the two sides of the region in question, then the electric fields are also different. In this way an emf appears in the open circuit and it is proportional to the difference between these fields [in full agreement with Eq. (3)], and when the circuit is closed electric current flows.

This model situation can be realized experimentally in a variable-gap semiconductor with a coordinate-dependent ratio of the effective masses of the light and heavy holes (for example, in $\text{Si}_x\text{Ge}_{1-x}$) under the conditions of inhomogeneous impurity generation of nonequilibrium holes.

In connection with this mechanism of the appearance of an emf we should mention that the emf can appear even in a unipolar semiconductor with one type of carrier ($k = 1$) and with a coordinate-independent average carrier energy. In fact, the above conclusion that such an emf cannot appear is based on the assumption that the Einstein relationship $u_k = e_k D_k / I_k$ applies; here, u_k and D_k are the mobility and the diffusion coefficients of carriers. If the Einstein relationship is not obeyed (this is possible if the symmetric part of the nonequilibrium distribution function is not of the Fermi type), then the ratio u_k/u_l for the left- and right-hand edges of the region of generation of nonequilibrium carriers will be different for the same average carrier energy. In this case, as in the presence of two types of holes, different electric fields will appear on the left and right of the generation region and, therefore (as shown in Ref. 7), contrary to the generally accepted ideas an emf appears in a unipolar medium with a constant average energy of carriers because nonequilibrium majority carriers are generated.

It should be pointed out that violation of the Einstein relationship in an inhomogeneous unipolar circuit may occur also because of a steep drop of the average energy of carriers in some part of the circuit when a special distribution of heating and cooling units is adopted. This may also give rise to an emf as a result of the mechanism discussed above. This emf includes a contribution from a change in the thermoelectric power a , which is different in the regions of rise and fall of the average carrier energy in such a circuit. These two factors taken together are the real reason for the appearance of the Benedicks emf in a unipolar semiconductor.

We shall now consider the possibility of the appearance of an emf in the presence of thermal effects and we shall do this by returning to the temperature approximation. It should be noted that the carrier temperature differs from the electrochemical potential $\tilde{\varphi}_k$ because it plays a dual role in Eqs. (1) and (2) since it occurs in these expressions both via $\tilde{\varphi}_k = \tilde{\varphi}_k(T_k)$ and directly in the form of the term $\alpha_k(dT_k/dx)$ (Ref. 13). This gives rise to an emf even in a unipolar medium and is responsible for the second term that is the cause of this emf.¹¹ However, in media with several types of carrier there are more opportunities for the appearance of different types of a thermo-emf because the emf is generated not only by the gradients of T_k , which occur explicitly in Eqs. (1) and (2), but also because of the gradients of $\tilde{\varphi}_k$, which appear due to the dependence of $\tilde{\varphi}_k$ on T_k .

One of such unusual thermoelectric effects is, for example, the appearance of a thermo-emf and of a thermoelectric current in an inhomogeneous circuit under the conditions of spatial homogeneous heating of carriers along the whole circuit ($T_k = \text{const} \neq T_0$, where T_0 is the constant temperature of phonons).

In describing this effect we shall use Eq. (4). Bearing in mind that the values of the chemical potentials of electrons and holes μ_n , and μ_p (measured from a constant shared level upward and downward, respectively) depend on the temperature T_n and T_p , we find that the emf due to the heating of carriers is

$$E = \frac{1}{e_p} \oint \frac{\sigma_n}{\sigma} \frac{d}{dx} (\delta\xi_p + \delta\xi_n) dx = \frac{e}{e_n} \oint \frac{\sigma_p}{\sigma} \frac{d}{dx} (\delta\xi_p + \delta\xi_n) dx \quad (6)$$

where

$$\delta\xi_k = \varepsilon_k - \varepsilon_{k0} = (T_k/T_0 - 1)\xi_{k0} + T_k[\ln(n_k/n_{k0}) - 3/2 \ln(T_k/T_0)];$$

$$\xi_k = \xi_k(T_k, n_k) = T_k \ln[n_k N_k(T_k)];$$

$$\xi_{k0} = \xi_k(T_0, n_{k0});$$

n_{k0} and n_k are the equilibrium and nonequilibrium carrier densities; $N_k(T_k)$ is the effective density of states in the relevant band (it is assumed that the investigated semiconductor is nondegenerate). If the density of the majority and minority carriers does not change during heating, it follows from Eq. (6) that the emf is described by the expression

$$E = -\frac{\vartheta_p}{e_p} \oint \frac{\sigma_n}{\sigma_n + \sigma_p} \left[\frac{dE_g}{dx} + \left(1 - \frac{\vartheta_n}{\vartheta_p}\right) \frac{d\xi_{n0}}{dx} \right] dx \quad (7)$$

where $\vartheta_k = (T_k - T_0)/T_0$ and where E_g is the band gap of the semiconductor. It is clear from Eq. (7) that in a closed circuit with an inhomogeneous doping and particularly in one with a variable band gap an emf may indeed appear when the heating of carriers is homogeneous along the whole circuit. If $T_n = T_p \neq T_0$, this is possible only in a variable-gap circuit [it is understood that naturally this requires a suitable inhomogeneous doping so that the value of $\sigma_n/(\sigma_n + \sigma_p)$ varies continuously]. Even if $E_g = \text{const}$, an emf may appear if the heating of electrons and holes is

different ($T_n \neq T_p$; in particular, $T_n \neq T_p = T_0$) and, consequently, the carrier mobility depends on the coordinate [the coordinate dependence of just the carrier density is insufficient, since then the quantity $\sigma_n/(\sigma_n + \sigma_p)d\xi_{n0}$ is not a total differential].

In spite of the very special nature of the situation discussed here, the possibility of the appearance of such a thermal-emf is of fundamental importance because the conditions needed for the generation of anomalous emf's may occur if not throughout the circuit then at least in some parts of it. For example, this thermo-emf is closely related to the familiar hot-carrier thermo-emf across a p - n junction.¹⁴

In fact, if we allow for the continuity of the quasi-Fermi levels of electrons and holes across a p - n junction, then an emf which appears in the case of homogeneous heating of carriers in the vicinity of a symmetric junction when the circuit is open and the temperatures T_n and T_p are identical, can be described by the following expression which is deduced from Eq. (6):

$$E_{pn} = \left(\delta\xi_p^{(n)} - \delta\xi_p^{(p)} \right) / \bar{e}_p, \quad (8)$$

which in the $n_k = n_{k0}$ ($k = n, p$) case gives the familiar result¹⁴

$$E_{pn} = U_{pn}(T_{p,n} - T_0) / T_0, \quad (9)$$

where $U_{pn} = [\xi_p^{(n)}(T_0) - \xi_p^{(p)}(T_0)] / e_p$ is the equilibrium contact potential across a junction (the upper indices identify the p - and n -type regions of the junction). However, it should be noted that an important condition in the derivation of Eq. (9) is the constancy of the densities of the majority and minority carriers during heating. However, the densities of carriers of one or the other kind can in fact vary with heating, so that the value of the emf may differ from that given by Eq. (9). In particular, if the generation-recombination equilibrium between the energy bands is controlled by direct band-band transitions, which is typical of semiconductors with a sufficiently narrow band gap, the heating of carriers causes their densities to rise in the same way as if they were heated together with the lattice. Then, if $T_n = T_p \neq T_0$, the positions of the quasi-Fermi levels of electrons and holes in the band gap coincide (as in the $T_n = T_p = T_0$ case) and they shift on increase in the difference ($T_{n,p} - T_0$). Consequently, the emf $E_{p,n}$ described by Eq. (8) vanishes. If the carrier temperatures at the external contacts are then equal to T_0 , we have the usual bulk thermo-emf E_T , which appears also when carriers are heated together with the phonons. The latter thermo-emf is much less than E_{pn} in Eq. (9) and has the opposite sign.

We shall now go back to our general case of a closed circuit in which an emf of arbitrary physical nature is generated. It is worth noting that such an electrical circuit can be divided into a region where an emf is generated and a region representing an external load only if the circuit has a section where $n_k = n_{k0}$ and $T_k = T_0$ for all kinds of carriers. It is this section that plays the role of an external load. If there is no such section, then in any selected part of the closed circuit the concept of the emf formed in this section becomes ambiguous and this is true also of the voltage drop across this section. For example, in the case of an ambipolar semiconductor when $T_n = T_p = T_0 = \text{const}$, we have the following obvious system of equations

$$\begin{aligned} jR &\equiv j \int_a^b \sigma^{-1} dx = \int_a^b \left(\frac{\sigma_1}{\sigma} \frac{d\tilde{\varphi}_1}{dx} + \frac{\sigma_2}{\sigma} \frac{d\tilde{\varphi}_2}{dx} \right) dx \\ &= - \int_a^b d\tilde{\varphi}_1 + \int_a^b \frac{\sigma_2}{\sigma} \frac{d}{dx} (\tilde{\varphi}_1 - \tilde{\varphi}_2) dx \\ &= \Delta\tilde{\varphi}_1 + E_1 = - \int_a^b d\tilde{\varphi}_2 + \int_a^b \frac{\sigma_1}{\sigma} \frac{d}{dx} (\tilde{\varphi}_2 - \tilde{\varphi}_1) dx = \Delta\tilde{\varphi}_2 + E_2. \end{aligned} \quad (10)$$

If by a section of a circuit we understand the whole closed contour ($r = R$), then $E_1 = E_2 = E$ [compare with Eq. (3)]. It is clear from Eq. (10) that if at the points a and b there is no carrier equilibrium ($\tilde{\varphi}_1 \neq \tilde{\varphi}_2$), then in general we have $\Delta\tilde{\varphi}_1 \neq \Delta\tilde{\varphi}_2$ and, consequently, $E_1 \neq E_2$. However, if in spite of nonequilibrium we have $\Delta\tilde{\varphi}_1 = \Delta\tilde{\varphi}_2$ then it would seem that the separation of the quantity jR into a voltage drop $\Delta\tilde{\varphi}_{ab}$ and an emf E_{ab} is unambiguous, the readings of a voltmeter connected between the points a and b do not give $\Delta\tilde{\varphi}_{ab}$. This is due to the fact that a separate emf appears in this case in the voltmeter circuit and this emf is due to nonequilibrium conditions. An ideal voltmeter is a device which does not alter the current in the measuring circuit (which means that the resistance of the voltmeter should be infinite), does not influence the carrier nonequilibrium, and does not develop its own emf. From all this it follows that the concept of a voltage drop can be introduced only for parts of a circuit between the points with equilibrium carriers and the voltmeter must be connected to these points. The voltage drop should then be the quantity $\Delta\tilde{\varphi}_{ab} \equiv \Delta\tilde{\varphi}_1 \equiv \Delta\tilde{\varphi}_2$, which is measured directly by the voltmeter. This quantity is equal to the drop of

the electrochemical potential of carriers between the points a and b , which is the same for all the carrier subsystems (irrespective of whether the electrochemical potentials of different carriers are the same within the investigated region). In the case of an electrical potential, its drop $\Delta\varphi_{ab}$ differs from that measured by the voltmeter $\Delta\tilde{\varphi}_{ab}$ by an amount $\Delta\mu_{ab}$, which is not equal to zero for an inhomogeneous circuit.

It follows from the above discussion that in the case of a unipolar semiconductor with the Fermi-type symmetric part of the distribution function, when the emf is related only to an inhomogeneity of the temperature distribution, the voltage drop should strictly speaking be determined between points at the same temperature. Clearly, if the intrinsic thermo-emf of a voltmeter vanishes, this voltmeter gives a reading of $\Delta\tilde{\varphi}_{ab}$ between any points and in the more usual general situation this can naturally be called the voltage drop. It should be pointed out that in the traditional approach to the definition of the thermo-emf it is $\Delta\tilde{\varphi}$ which is implied and not $\Delta\varphi$. This is attributed in Ref. 3 to the fact that the quantity $\Delta\varphi$ at the contacts has a discontinuity, whereas $\Delta\tilde{\varphi}$ is continuous. However, in fact $\Delta\tilde{\varphi}$ may also have a discontinuity (this is true if the conductivity of the contact itself is finite). In this case the jumps $\Delta\varphi$ may be associated with their own emfs influencing the readings of the instrument (as observed in the case of a hot-carrier p - n junction if the contact is understood to be the whole p - n junction region where the heating takes place). Consequently, in accordance with the conclusions reached in the present paper, we can find the emf if we determined $\Delta\tilde{\varphi}$ at the ends of a region which includes all the discontinuities of the electrochemical potentials of carriers of each kind.

All this is valid not only in the case of finite but also in the case of infinitesimally short sections of the circuit. Therefore, if an external voltage is applied to some part of a circuit and inside this part there are nonequilibrium carriers capable of creating an emf (this nonequilibrium state may be induced, in particular, by the applied voltage itself), then the electric field at the internal points in this part cannot be separated unambiguously into the purely “external” field and the “internal” (“nonequilibrium built-in”) field, which is associated with the generated emf. Similarly, a change in the electrical potential inside the medium on appearance of a nonequilibrium creating an emf cannot be interpreted as the emf itself (compare with Ref. 4), but outside the medium the emf is an indeterminate and directly measurable quantity.

An analysis of the process of formation of an emf given above thus provides a clear physical picture of the possible mechanisms and the conditions for the appearance of an emf of any nature in arbitrary electrical circuits with nonequilibrium carriers and it provides definite procedures for the calculation of such emf’s.

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Translated by A. Tybulewicz